Pilot Plant Studies on the Extraction of Antimony Metal from Lower Grade Krinj Stibnite Ore

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Summary: Antimony is a silvery white, brittle and crystalline solid which is extensively consumed in lead acid batteries, antimonial lead alloys, flame retardants and a variety of metallic products. The antimony content of commercial ores range from 5-60% and determines the method of extraction, either pyrometallurgical or hydrometallurgical. The present study focuses on pilot plant scale extraction of antimony metal from lower grade stibnite ore of Krinj (Chitral) without the use of iron scrap, thus eliminating the second step of iron removal in conventional direct reduction method. A tilting gas fired furnace with digital temperature control system and a heat recuperator was designed to optimize the operating parameters for extraction of antimony metal. Weight ratios of flux and reductant, operating time and operating temperature were optimized. Highest percentage recovery and purity were achieved using soda ash as a flux, at a temperature of 900 °C for 2 hours.

Key Words: Antimony, Pyrometallurgy, Gas Fired Furnace, Heat Recuperator.

Introduction

World reserves of antimony are estimated to be 2.10 million metric tons. Approximately 95% of the world's primary antimony is mined in China, which has the world's largest reserves [1]. In Pakistan several showings of antimony occur in the salt range, Kurram valley, near Khuzdar and in Kharan district but the main deposits are located near Qila Abdullah (Pishin District) and Krinj (Chitral district). In Qila Abdullah the main deposit is 24 km North East of Qila Abdullah. Antimony content in the ore is 5-30%. The Krinj deposits are located in the western part of Karakorum block which is about 18 km North of Chitral town. Antimony content varies from 29-38%. The total reserves in Krinj deposits are estimated to be 60,000 tones [2].

The world's supply of antimony comes mainly from the sulphide mineral stibnite (Sb_2S_3), minor amounts coming from such oxidized ores as cervantite ($Sb_2S_3.Sb_2O_5$), valentinite (Sb_2O_3) and kermesite ($2Sb_2S_3.Sb_2O_3$). Broadly, the methods in use to recover the metal from ore can be classified under three headings: The first method is volatilization followed by reduction. The second method is direct production of metal from ore by reverberatory, blast, shaft, cupola and crucible furnaces. The third method is leaching followed by electrolysis of a solution of the metal in an alkaline medium [3].

Several scientists have investigated the extraction of antimony from stibnite by different methods. T. Lager [4] reviewed the current processing technologies for antimony bearing ores. M. A. Bhatti [5] evaluated the mineralogical and liberation characteristics of stibnite ore of Chitral.

Based on the mineral assemblage and the texture characteristics, the ore was found amenable to beneficiation by froth floatation technique. M. Riaz [6] carried out the floatation studies of low grade stibnite ore of Krinj (Chitral). The antimony contents in stibnite ore were upgraded from 20% to 35% by wet sieving and further upgradation was achieved by using a combination of coaltar-coaltar creosote collectors in froth floatation process. I. Ahmad [7] recovered 60% Sb_2S_3 with 97% antimony by using a brick kiln for liquation of stibnite. M. I. Bhatti [8] extracted antimony by direct reduction of stibnite ore of Chitral in the presence of iron scrap, and fluxing agents like NaCl, Na_2SO_4 and $NaHSO_4$. Optimum recovery of the metal ranged from 92-94% with a purity of about 95%. J. Guang [9] obtained antimony recovery of 97% with crude antimony grade of 96.45% and sulfur fixing rate of 98.61% by using a smelting temperature of 880 °C for 2 hours employing zinc oxide as sulfur fixing agent. S. Ubaldini [10] obtained electrodeposited pure antimony metal from stibnite ore by alkaline leaching in sodium sulphide and sodium hydroxide solutions. P. Balaz [11] leached stibnite with a basic solution of sodium hydrogen sulfide and found that intensification of leaching by mechanical activation accelerated the process by tenfold. E. Smincakova [12] calculated the apparent activation energy and apparent order of stibnite reaction with the solution that contained sodium hydroxide to be $E_a \approx 50.7$ kJ mol^{-1} and $n \approx 1$, respectively. H. Loufty [13] carried

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out hydrometallurgical treatment of stibnite ore, based on leaching with acids, precipitation and electro-deposition of metal. T. Mahlangu [14] investigated the reductive leaching of stibnite in hydrochloric acid. The leaching process achieved desulphurization in excess of 95% to produce elemental and dissolved antimony, ferrous ions and hydrogen sulphide gas. A. E. Torma [15] reduced stibnite by leaching in hydrochloric acid solution in the presence and absence of sulfur acceptors at temperature of 200-600 ^{o}C, thus achieving 98.0-99.5% pure metal. F. P. Gudyanga [16] achieved over 80% reduction of stibnite to antimony and hydrogen sulfide using an acidified solution of chromium ions in a chloride medium. M. Copur [17] found the optimum conditions for 99% dissolution of stibnite in hydrochloric acid solution to be reaction temperature, 70 °C; solid-to-liquid ratio, 0.125; acid concentration, 37%; mean particle size, 0.1061 mm; stirring speed, 700 rpm; and reaction time, 60 minutes.

The present study focuses on direct production of metal from ore without the use of iron scrap, thus eliminating the second step of iron removal in conventional reduction method.

Results and Discussion

The Krinj stibnite ore which was used in our studies had an antimony content of 21.21%. Soda ash, gypsum, sodium sulphate, calcium carbonate and charcoal used were of commercial grade.

The lump ore was crushed in a jaw crusher and ground in a disc grinder. The ground stibnite ore, flux, and charcoal were mixed uniformly in a blender. The final mixture was smelted at controlled temperature in a tilting gas fired furnace. After smelting the molten metal along with slag was poured into sand moulds. When the metal and slag cooled and solidified, then mould was broken to get pure metal.

1) Effect of Type of Flux:

Four types of fluxes were used to analyze the effect of each type of flux on percentage recovery and purity of the metal. Soda ash, gypsum, sodium sulphate and calcium carbonate were tried. Weight ratios of 5 parts of ore, 5 parts of flux and 1 part of charcoal were used. Smelting was carried out at 900 ^{o}C for 2 hours. It was found that only soda ash gave a percentage recovery of 77.32% of metal with a percentage purity of 96.12%. No metal could be extracted with the remaining fluxes at theses conditions. Therefore the remaining parameters were optimized using soda ash as a flux.

2) Effect of Weight of Flux

Weight of flux is one of the cost controlling factors in the process, so it was varied to determine an optimum value. It can be seen from Table-1 and Fig. 1, that keeping the temperature and time constant, a weight ratio of 1: 0.70: 0.14 respectively for ore, flux and charcoal, gave the highest yield and purity of metal.

Table-1: Effect of Weight of Flux on Extraction of Antimony Metal Temperature: 900 ^{o}C, Time: 2 hours.

S.No	Ore: Flux: Charcoal	Recovery (%)	Purity (%)
1.	1 : 0.40 : 0.08	No recovery due to low amount of reductant	No recovery due to low amount of reductant
2.	1 : 0.70 : 0.14	81.10	98.78
3.	1 : 1.00 : 0.20	77.00	93.96
4.	1 : 1.30 : 0.26	65.10	97.83

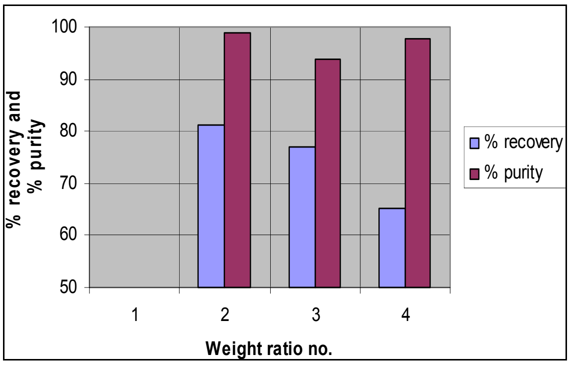

Fig. 1: Effect of Weight of Flux on Extraction of Antimony Metal.

3) Effect of Weight of Charcoal

In order to see the effect of weight of charcoal on recovery and purity of metal, it was varied below and above the optimum value of weight ratios obtained in Table-1. Thus it can be seen from Table-2 and Fig. 2, that keeping the temperature, time and ratio of ore and flux constant, variation in ratio of charcoal below and above the previously optimized value, did not increase the recovery or purity of metal.

Table-2: Effect of Weight of Charcoal on Extraction of Antimony Metal Temperature: 900 ^{o}C, Time: 2 hours.

S.No	Ore: Flux: Charcoal	Recovery (%)	Purity (%)
1.	1 : 0.70 : 0.07	66.95	98.05
2.	1 : 0.70 : 0.14	81.10	98.78
3.	1 : 0.70 : 0.21	62.24	98.47

4) *Effect of Smelting Time*

Smelting time has a direct influence on the recovery and purity of metal [8]. Excessive smelting time can result both in loss of the metal due to vaporization and loss of fuel, thus making the process uneconomical. Therefore optimum smelting time was determined for the process. It can be seen from Table 3 and Fig. 3 that keeping the temperature and ratio of raw materials constant, a smelting time of 2 hours gave the highest recovery and purity of the metal.

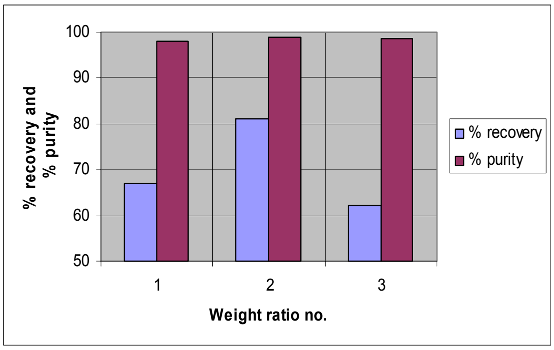

Fig. 2: Effect of Weight of Charcoal on Extraction of Antimony Metal.

Table-3: Effect of Smelting Time on Extraction of Antimony Metal Temperature: 900 ^{o}C, Ore: Flux: Charcoal; 1: 0.70: 0.14.

S.No	Time(Hours)	Recovery (%)	Purity (%)
1.	**0.5**	**54.41**	**98.76**
2.	**1.0**	**76.38**	**92.33**
3.	**1.5**	**74.18**	**92.20**
4.	**2.0**	**81.10**	**98.78**

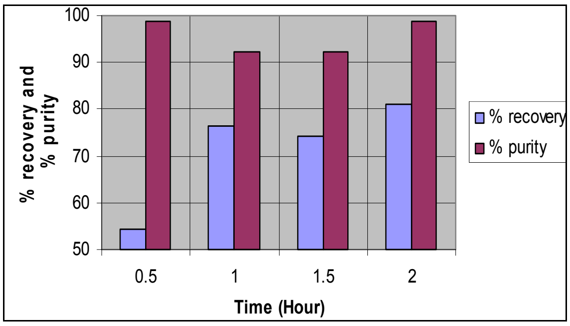

Fig. 3: Effect of Smelting Time on Extraction of Antimony Metal.

5) *Effect of Smelting Temperature:*

Using a higher temperature for the process, results in higher fuel consumption. So an optimum smelting temperature was necessary to be determined for saving extra fuel cost. It can be seen from Table-4 and Fig. 4, that keeping time and ratio of raw materials constant, a smelting temperature of 900 ^{o}C for 2 hours gave the highest recovery and purity of the metal.

Table-4: Effect of Smelting Temperature on Extraction of Antimony Metal Time: 2 hrs, Ore: Flux: Charcoal; 1: 0.70: 0.14.

S.No	Temperature (°C)	Recovery (%)	Purity (%)
1.	**800**	**53.75**	**95.70**
2.	**900**	**81.10**	**98.78**
3.	**1000**	**69.78**	**98.33**

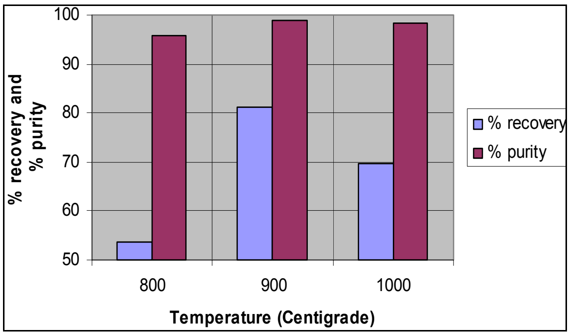

Fig. 4: Effect of Smelting Temperature on Extraction of Antimony Metal.

Experimental

Design of Tilting Gas Fired Furnace

In order to carry out the smelting of stibnite ore at controlled temperatures, a tilting gas fired furnace with heat recuperator system was designed. The furnace consisted of an outer mild steel shell which was internally lined with high alumina refractory castable. Ceramic wool insulation was provided in-between the shell and refractory castable. A graphite crucible of 10-15 Kg capacity resting on a high alumina frustum was used for smelting purpose. The furnace could be tilted to pour the molten product in sand moulds. Natural gas was used as a fuel, while air was provided by a blower to aid in combustion. Air and gas were mixed in a burner nozzle.

Design of Recuperator

Recuperator is a heat exchanger that transfers heat of the hot fluid to the colder one without allowing them to mix with each other. Approximately 15% of fuel (natural gas) saving can be achieved by using a recuperator that preheats the air up to 400 ^{o}C. The percentage saving of fuel is proportional to the preheat temperature of air [18].

To recover the waste heat of flue gases from tilting gas fired furnace, a heat recuperator was designed. It consisted of a conical bottom and two pipes, the smaller being immersed in the larger one. In between the annular space of two pipes, a screwed path was provided for increasing the residence time of air and the heat transfer area. The conical bottom of recuperator guided the flue gases to pass through the internal pipe which caused its walls to get heated. Air from blower was heated while passing though the screwed path in annular space. This preheated air was then mixed with the natural gas and fed to the furnace.

Instrumentation and control

An R-type thermocouple was installed in the furnace for temperature detection. Its output was fed to a digital temperature controller. There the desired temperature was already set. The error generated in the controller due to the difference in set point temperature and measured temperature, caused a solenoid valve on natural gas line to open or close. At the same time the error value caused the blower to start or stop. Thus as the temperature exceeded the set point value, the controller simultaneously closed the solenoid valve and stopped the blower. So a stable temperature was maintained in the furnace.

Conclusion

The present study focused on pilot plant scale extraction of antimony metal from lower grade stibnite ore of Krinj (Chitral) without the use of iron scrap, thus eliminating the second step of iron removal in conventional direct reduction method. A tilting gas fired furnace with digital temperature control system and a heat recuperator was designed to optimize the operating parameters for extraction of antimony metal. Weight ratios of flux and reductant, operating time and operating temperature were optimized. It is thus concluded that using soda ash as a flux with weight ratio of ore, flux and charcoal of 1: 0.70: 0.14 respectively, at a temperature of 900 °C for 2 hours resulted in the highest percentage recovery and purity of antimony metal.

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